Anisotropic crystal of the δ-BiB_3O_6 investigated by vibrational spectroscopy

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Abstract. The vibrational spectroscopy has been applied to investigate the structure the BiB3O6 (BIBO) crystal. Based on the experimental results, the total set of phonons mode of the polarized Raman spectra was proposed. To verify the obtained experimental data have been performed theoretical calculation in software package LADY.

1. Introduction

BiB_3O_6 (BIBO) has excellent optical nonlinear properties for to conversion fervency in the solid state lasers [1]. It is most effective in the optical range UV and visible light which have widely been used in medicine, signal progressing. BIBO have large nonlinear optical coefficient due to its structure and non-hydroscopic nature [2].

Long time thought that BiB_3O_6 have only alpha phase with space group symmetry C2. [3] Recently have been found new six phase of this compound. More extensively known and studied phase is α-BiB_3O_6, which build from chain bounded triangles [BO_3] and tetrahedrons [BO_4] in range 1:2. β- BiB_3O_6 is metastable phase and it can undergo the phase transition in other phase at the high temperature. As α - BiB_3O_6, β - BiB_3O_6 consist of chain bounded triangles [BO_3] and tetrahedrons [BO_4] in range 2:1. The first principles simulation showed that the main contribution in nonlinearity comes from [BO_4] tetrahedral units. Therefore, γ and δ – BiB_3O_6 attract the great interest due to the features of their structures (Figure 1) which are exclusively consisting of the chains of bounded tetrahedrons [BO_4].

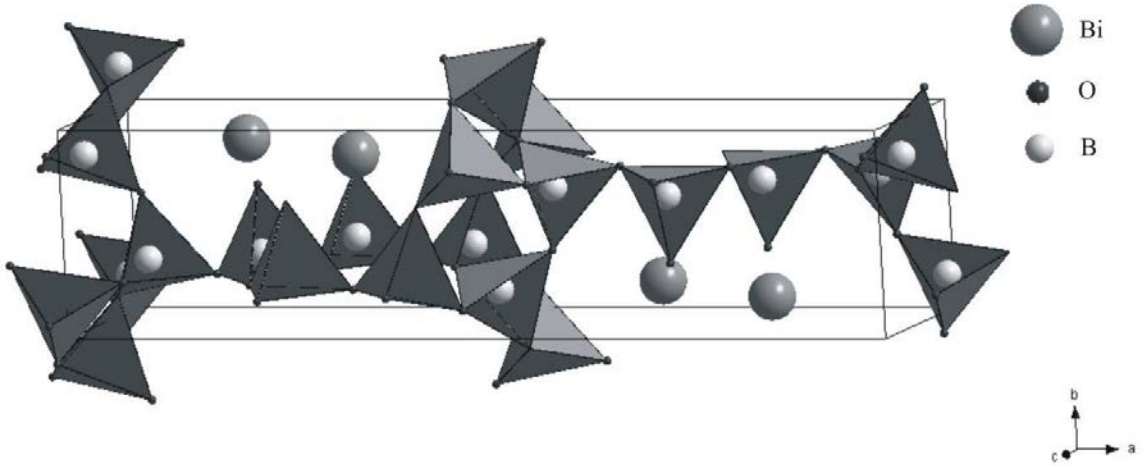

Figure 1. The crystal structure of δ–BiB_3O_6.

Since γ – BiB_3O_6 have inversion center, subject of the present research work is δ – BiB3O6. The symmetry space group of orthorhombic δ - phase is $Pca2_1$ (Z=4). The expansion of the total vibrational representation in the Brillouin zone center for the δ phase has the following view: $\Gamma V_{ibr} = 30A_1 + 30A_2 + 30B_1 + 30B_2$, acoustic and optic modes: $\Gamma_{acoustic} = A_1 + B_1 + B_2$, $\Gamma_{optic} = 29A_1 + 30A_2 + 29B_1 + 29B_2$.

2. Experiment

The samples have been obtained same as described in the paper [4]. The assembling is spectrometer Horiba Jobin Yvon T64000 equipped with a liquid nitrogen cooled charge coupled device detection system in subtractive dispersion mode in 10 to 1600 cm^{-1} range. The spectra were recorded in the backscattering geometry. It was used notation. [4]

3. Results and discussion

To simulate the δ – BiB_3O_6 the vibrational spectrum package LADY was used. The program allows to obtain the full Raman spectrum using the model of „rigid-ion". The interatomic potential is considered as a sum of the short-range interaction potentials was taken in the Born–Mayer form:

$$V^{RIM}(r_{ij}) \frac{1}{2} \sum_{ij} \frac{Z_i Z_j}{r_{ij}} U(r_{ij}), \quad (1)$$

and of the of long range Coulomb electrostatic potentials:

$$U(r_{ij}) = \lambda \exp(-r_{ij}/\rho), \quad (2)$$

where r_{ij} is the interatomic distance and λ and ρ are the parameters characterizing of the short-range pair interionic interaction. Resulting model parameters were obtained by minimization of residual values of the simulated and experimental Raman frequencies using the Fletcher – Reeves method [5–7]. The values of λ, ρ and Z_{ij} are listed in Table 1.

Table 1. Parameters of the interatomic interaction potential:

Interactions	Radii of interaction, Å	□, aJ/Å^2	□, Å
Bi – O	0–3.00	350.00	0.300
B1 – O	0–1.50	321.60	0.210
B2 – O	0–1.60	400.60	0.220
B3 – O	0–1.60	345.30	0.199
O – O	0–3.00	242.80	0.245
Ion	Bi	B	O
Z(e)	2.00	1.80	-1.2333

The Raman active frequency is shown in Table 2 in comparison with experiment

Table 2. The calculated Raman active frequencies are shown in Table 2 along with the experimental dates

A_1			**A_2**		**B_1**		**B_2**	
exp.		calc.	exp.	calc.	exp.	calc.	exp.	calc.
TO	LO							
1116	1097	1121	1076	1153		1212		1278
1081	1035	1093	1037	1119	1082	1132	1037	1132
1031	1007	979	1010	1090	1035	1023	1010	1029
996	975	959	978	981	997	949	997	965
959	935	908	944	945	955	938	956	929
919	907	894	905	912	919	910	936	905
864	865	789	864	805	897	854	880	892
807	783	752	784	755	863	803	784	786
783	727	721	728	751	813	749	727	737
752	650	697	709	730	783	732	665	689
726	607	634	607	648	753	648	607	647
639	530	598	558	606	727	618	515	623
606	515	552	534	553	607	575	499	563
530	502	510	514	529	578	533	468	518
499	467	490	501	511	531	504	415	483
467	416	447	466	490	515	497	393	459
415	394	428	417	428	500	432	327	442
393	329	384	393	416	467	421	312	400
328	310	345	330	382	415	392	304	383
303	256	320	313	332	394	347	249	338
272	244	274	255	310	327	319	226	307
228	235	255	246	262	304	299	204	280
186	225	221	226	227	245	267	185	240
175	194	159	196	191	229	229	177	185
122	165	128	126	170	184	156	166	135
97	120	100	110	94	123	116	123	119
71	88	69	89	89	116	89	112	94
67	69	46	68	70	97	76	98	66
46	49	18	51	54	71	55	69	35
			49	44	68		45	

Since the BO_4 bounded with B-O in crystal is not ideal we can observe a large number of vibrations in the range > 650 cm^{-1}. For this reason the whole spectrum is reached of lines. The simulations is shown that about 40 active modes appear in the range >650 cm^{-1} for the different position of the polarization.

The bands below 150 cm^{-1} are related with Bi translation vibrations. The lower wavenumber range of 150–350 cm^{-1} contains translational, rotational and mixed vibrations of BO_4 tetrahedra. Bands in the 350–650 cm^{-1} range are related with the distorted ν_2 and ν_4 BO_4 bending modes. Generally, frequency of ν_4 vibration should be above that of ν_2 vibration [8].

In the Figure 2 a,b is presented LO-TO splitting in depending on the different position of the polarization is presented. The lines corresponding to B_1 and B_2 modes are presented on Figure 3 a,b.

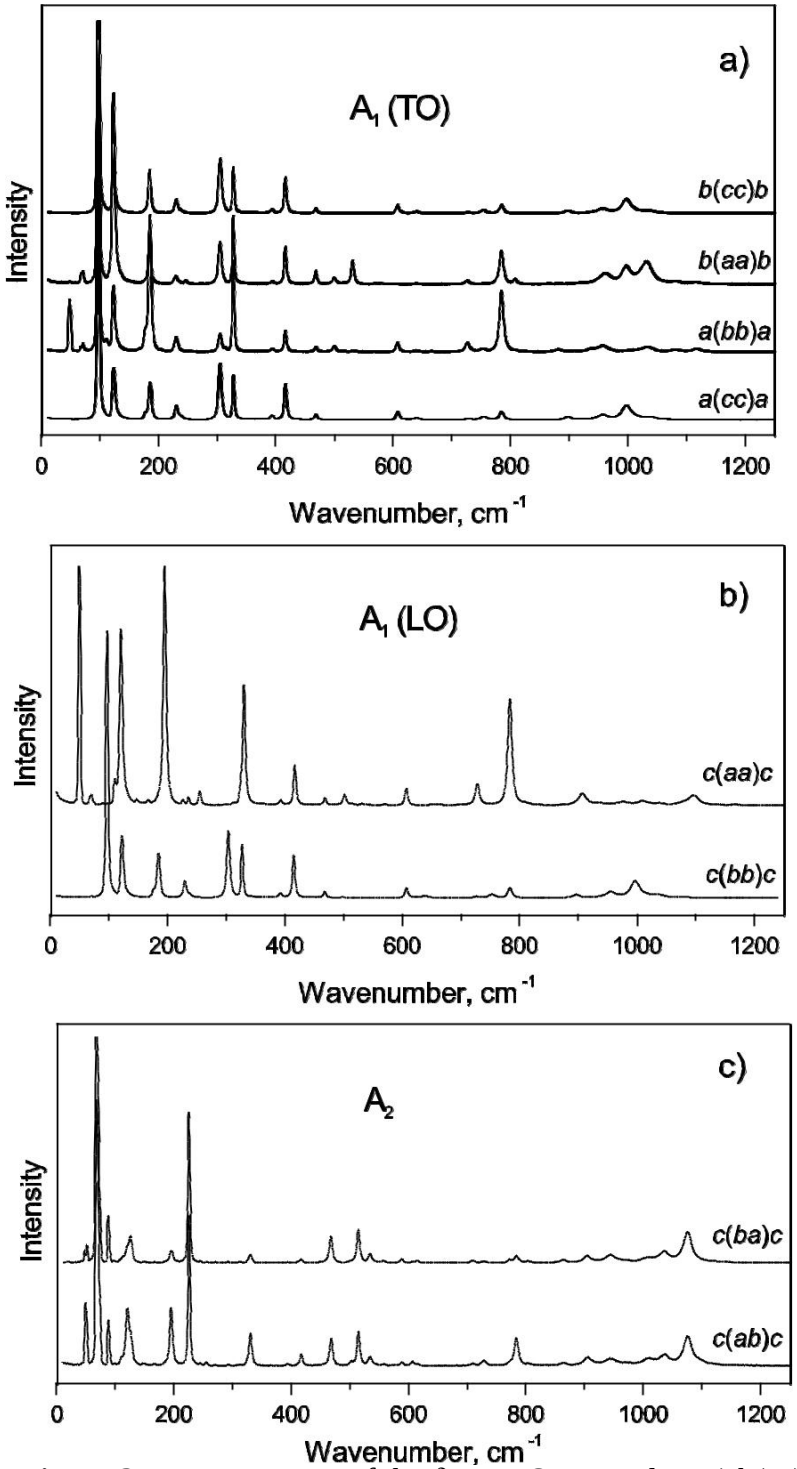

Figure 2. Raman spectra of the δ–BiB_3O_6 crystal at: a) b(cc)b, b(aa)b, a(bb)a, a(cc)a b) c(aa)c, c(bb)c, c) c(ba)c, c(ab)c geometries

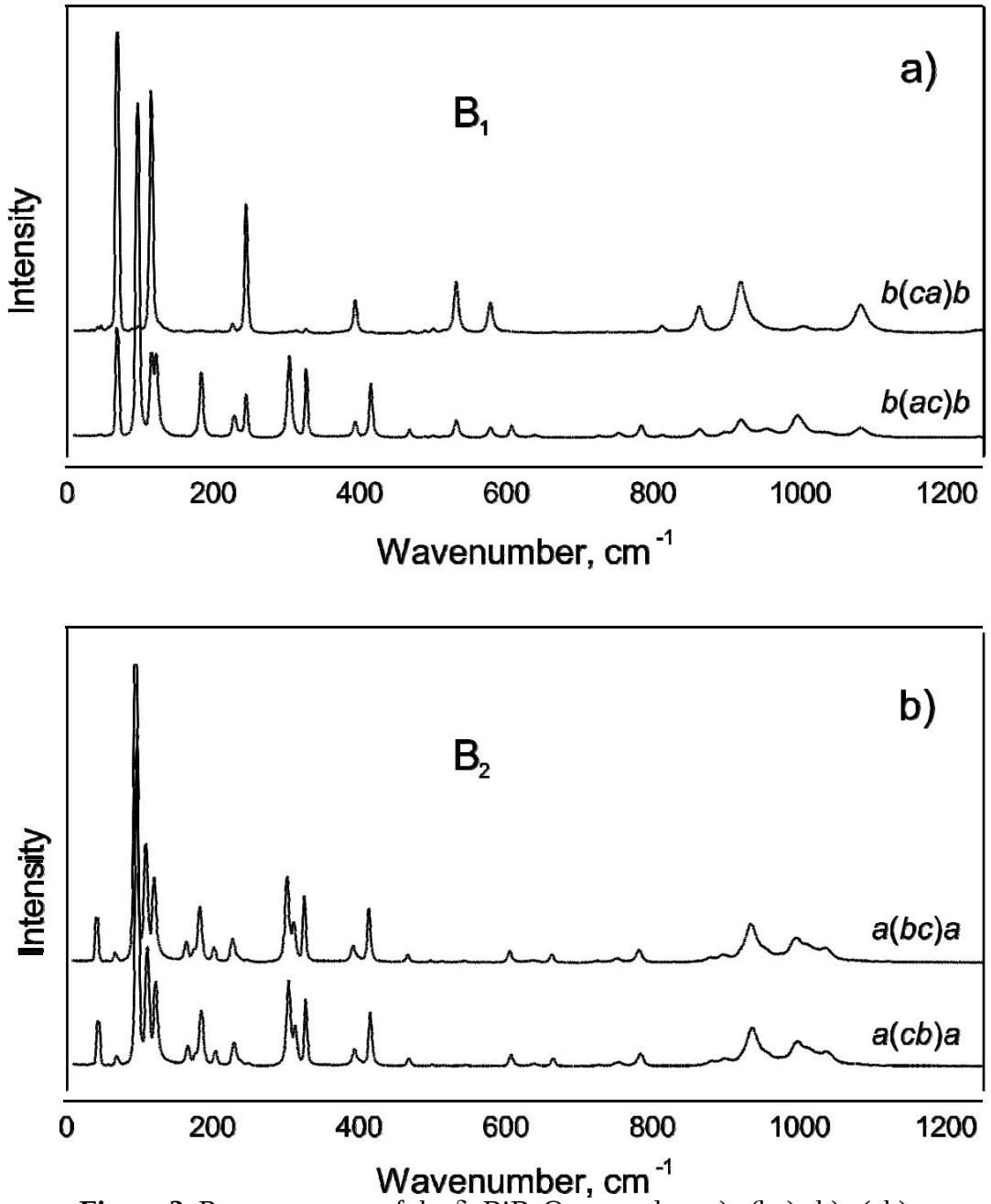

Figure 3. Raman spectra of the δ–BiB_3O_6 crystal at: a) a(bc)a b) a(cb)a

4. Conclusion

The polarization selection rules, lattice dynamic simulations and number of the spectral lines are in the good agreement with experiment. The full set of experimental Raman spectra polarizations is presented. The vibration modes are classified to corresponding Raman bands.

Acknowledgments

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